Why Glass Is a Good Host for Hazardous Waste

A look at the structural factors that make it useful for containing heavy metal oxides

GLASS is an excellent host for permanent sequestering of heavy metal oxides found, for example, in ashes from hazardous waste incineration, contaminated soils, arc furnace dust, and electroplating wastes. The heavy metals of concern here are arsenic, barium, cadmium, chromium, lead, selenium and silver. (Mercury is also on the list, but is not retained in a glass melt.)

These metals in oxide form are compatible with the oxide matrix of silica and are bound therein, protected from attack (dissolving) by water and common acids. This property of insolubility allows glass to be so useful in materials of daily living, such as containers and windows.

A solid is said to be in the vitreous state when it has retained the general atomic structure, including free volume, that it had when it was liquid. Glass is a subdivision of the vitreous state, defined for this paper as follows:

Glass is an amorphous inorganic substance typically formed by fusion of sand (silica) with a flux (soda) and a stabilizer (lime, alumina) so that a mass is produced that cools to a rigid condition without crystallization. The free volume is commonly about 15 percent.

Quartz (crystalline silica) can be made into vitreous silica just by heating it to about 1670°C (3200°F). There is a pronounced volume expansion in the course of the conversion, but no corresponding shrinkage on cooling. The new solid, vitreous silica, has the open atomic structure that it had when it was a liquid.

Vitreous silica could be used as a host for the heavy metal oxides but has the disadvantage of high melting point and high viscosity. The viscosity and working temperature can both be lowered markedly by adding fluxes, soda (Na_2O) and lime (CaO). Soda especially breaks the strong silicon-oxygen-silicon bonds in the continuous four valent (four-way) sponge-like silica matrix. (See Fig. 1.)

There are now two free-swinging monovalent endings in place of the original bridging oxygen, thus lowering the viscosity.

Calcia can also break the bridging oxygen bonds. Calcium doesn't fully let go, however, because it is divalent. (See Fig. 2.)

In industrial glass practice, soda and calcia are used in combination for breaking bonds. Standard container and window glasses have the following composition:

	wt. %	Glass Melting Temp.
Silica	73.5	
Soda	14.5	2500°F
Calcia	10.5	1315°C
Alumina	1.5	

Note particularly that the total of the fluxes, soda and calcia, is about 25 percent. This retains three valence bonds for each silicon. The resulting glass has excellent resistance to attack by both water and acids.

When a soda-lime-silica glass is exposed to groundwater, the atoms of sodium in the surface layer are dissolved and replaced by hydrogen atoms.

Groundwater usually contains dissolved calcia, magnesia, and ferrous oxide, which immediately displace the hydrogen in pairs to supply a healing effect, protecting against further attack by water. (See Fig. 3.)

Alumina very markedly improves the resistance of glass to water attack. Alumina forms a viscous hydroxide gel a few molecules thick that impedes diffusion of soda outward and water inward.

Alumina also inhibits the crystallization of silica-calcia (devitrification) because it does not fit in the crystalline lattice and stops the growth of such crystals.

When present in larger ratio, alumina binds to calcia/ferrous oxide to form another compatible vitreous system.

Glassmaking ingredients can be considered in four classes, spoken of as RO_2, R_2O, RO, and R_2O_3 and presented in Table 1. Substitutions of ingredients within each class can be made without upsetting the vitreous state.

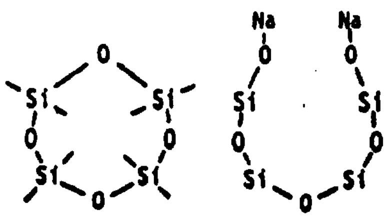

Fig. 1—Silicon-oxygen bond broken by soda.

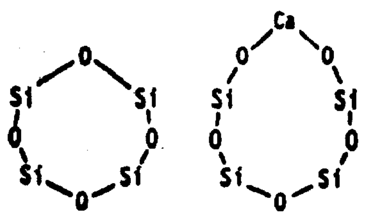

Fig. 2—Silicon-oxygen bond broken by calcia.

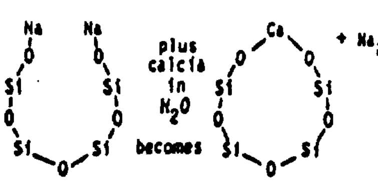

Fig. 3—Healing effect of calcia, magnesia, and iron oxide.

TABLE 1

RO_2 Network Formers	R_2O Fluxes Bond Breakers	RO Stabilizers Healers	R_2O_3 Crystallization Inhibitors
SiO_2	Na_2O	CaO ZnO	Al_2O_3
TiO_2	K_2O	MgO MnO	Fe_2O_3
ZrO_2	Cs_2O	BaO AgO	As_2O_3
	Li_2O	CdO CoO	B_2O_3 (limited)
		FeO PbO	Cr_2O_3 (limited)

TABLE 2—Sample TCLP Test

	As	Ba	Cd	Cr (ppm)	Pb	Hg	Se	Ag
Allowable max. conc. in leachate	5	100	1	5	5	0.2	1	5
Sample TCLP test	ND	0.002	0.005	0.01	ND	ND	0.3	0.01

ND = None Detected

Some glassmaking ingredients do not participate in forming the vitreous matrix, but instead precipitate out in microcrystalline or colloidal form where they act as light diffusers, when above a certain percentage and slowly cooled or reheated. The common ones are calcium phosphate, calcium fluoride, tin oxide, colloidal gold, colloidal copper, cadmium/selenium sulfide, iron sulfide, titanium dioxide, chromium silicate.

The presence of opalizing components does not interfere with the sequestering action of the glass as long as there is enough glass to surround and isolate each crystallite.

Various of the glassmaking ingredients cause the glass to be colored. They are: cobalt oxide, dark blue; copper oxide, bright blue; chromium oxide, green; manganese oxide, purple; iron sulfide, amber; iron oxide, green; cadmium sulfide, yellow; cadmium-selenium sulfide, red; copper, colloidal, red; silver oxide, weak yellow; uranium, yellow-green fluorescent.

Sulfate above 1 percent is immiscible with silica glass and separates out on the surface as molten sodium sulfate. Addition of a reducing agent (charcoal) converts the sulfate to sodium oxide, which enters the glass, and sulfur dioxide, which exits as a gas.

Chloride is immiscible with glass above 1 percent and floats on the surface as a molten salt.

Glass structure is like a sponge, having about 15 percent free volume throughout. When heavy metal oxides are added while molten, the glass matrix has no difficulty bending locally on an atomic scale to accommodate the added material. Within limits, the added materials stay within the vitreous structure, surrounded and protected by the silica and alumina/calcia.

Investigators at Atomic Energy of Canada Ltd. in 1955 moved to use this property to sequester radioactive fission products into a glass matrix and published in 1955-1960 excellent papers on their work.[1] They used a batch containing 85 percent nepheline syenite and 15 percent lime (CaO) as their host glass composition. The final glass was: SiO_2, 51%; Al_2O_3, 20.4%; CaO, 15%; Na_2O, 8.5%; K_2O, 4.3%; other, 0.8%.

This is an excellent composition, proven by 20 years of exposure of their radioactive glass blocks to groundwater, being buried five feet deep in wet soil.

Interest in the glass method of sequestering radioactive fission products has spread and is being used in production routinely in France.

In the EPA-RCRA hazardous waste management program, vitrification is a matter of some urgency. Vitrification has been chosen as the best demonstrated available technology for various waste streams, accentuated by the landfill disposal ban taking effect May 8, 1992.

The purpose of vitrification is to make the heavy metals so leach resistant that they are no longer in the EPA regulatory sphere. The situation is dynamic in that the Court of Appeals struck down the derived-from rule that EPA was using to keep in the EPA net produced glass that had been associated with hazardous waste destruction furnaces, such as in the Molten Glass Furnace Process.[2] EPA reinstated the rule on an interim basis until April, 1993, intending in the meantime to relax the rule.

The foregoing problem applies to hazardous wastes which have been processed commercially. However, individual plants can process their own secondary materials, making the mineral portions into glass, without EPA jurisdiction.[3]

EPA for a long time used the Extraction Procedure Test (EP Tox) for determining the leachability of heavy metals from a substrate. The leaching solution was weak acetic acid. Glass is perfect as a host for heavy metal oxides by this test.

Recently, the test was changed to Toxic Characteristic Leaching Procedure (TCLP), which additionally looks for organic materials. There are no organic materials in glass, so that portion of TCLP can be skipped.

The defect in the TCLP is that its authors included an 18-hour tumbling step in contact with the solution, which artificially abrades the few-molecules-deep healed surface of the glass, exposing fresh glass continuously. When the glass is properly compounded and melted, even this does not cause the glass to test out of limits. But the tumbling also makes microchips, which should be centrifuged out of the filtrate before testing by a flame method (AA and ICP).

A typical TCLP result for a production glass is given in Table 2. ✩

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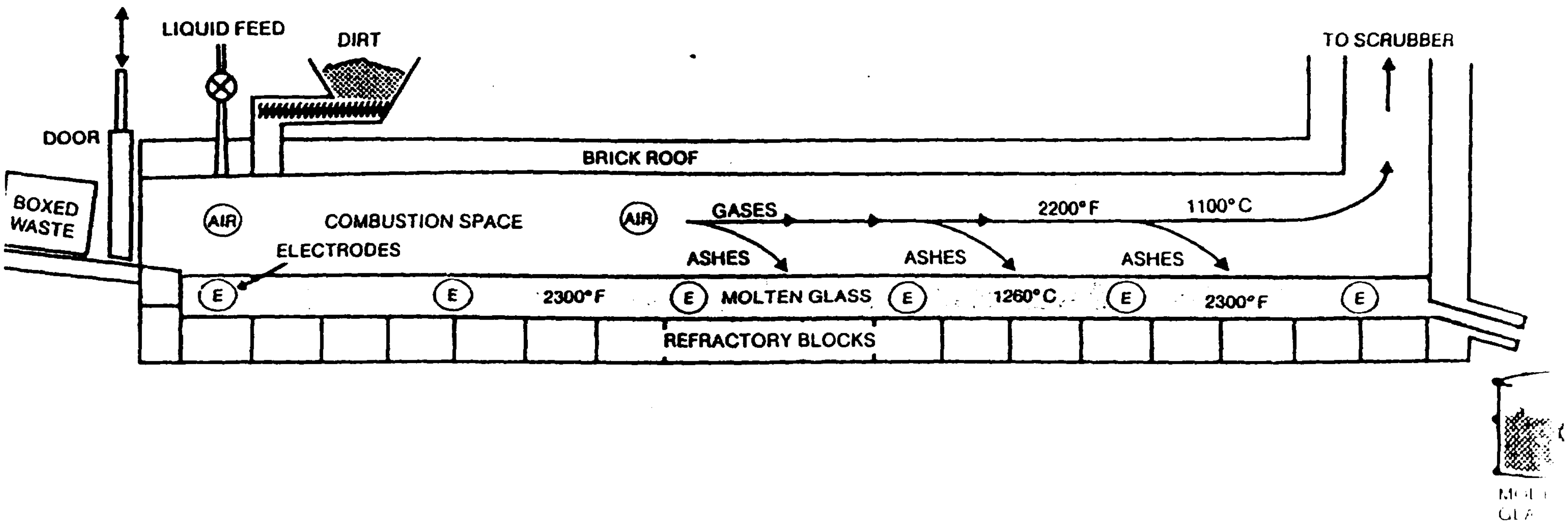
2. U.S. Patent 4,299,611, L. Penberthy, 1981, Method for Converting Hazardous Material to a Relatively Harmless Condition.

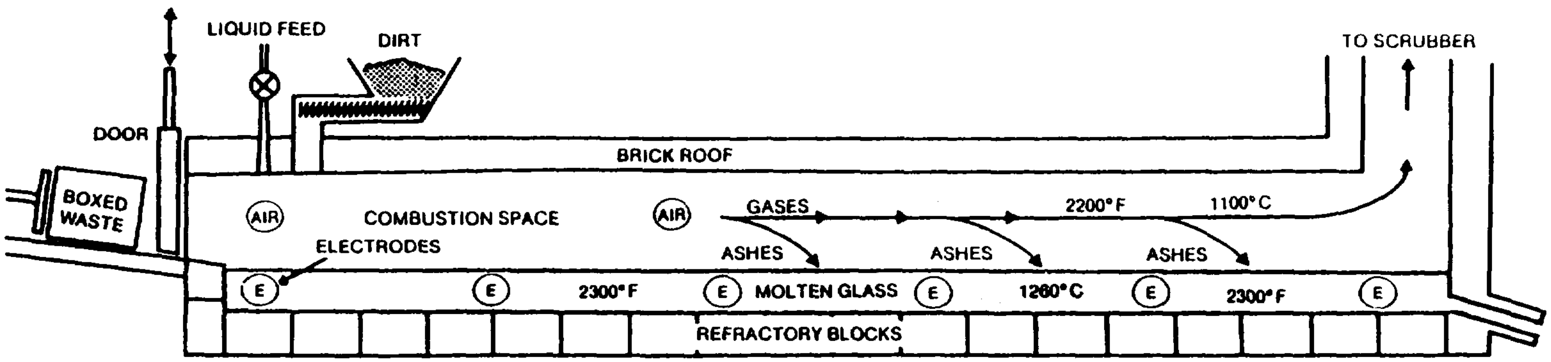
3. The Impact of the 1987 Court Decision Regarding EPA's Secondary Materials Regulatory Claim. L. Penberthy, Aug. 1991.


LIQUID FEED
DIRT
TO SCRUBBER
DOOR
BRICK ROOF
BOXED WASTE
AIR
COMBUSTION SPACE
AIR
GASES
2200° F
1100° C
ELECTRODES
ASHES
ASHES
ASHES
E
E
2300° F
E
MOLTEN GLASS
E
1260° C
E
2300° F
E
REFRACTORY BLOCKS

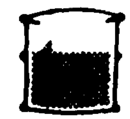
The electric mol. . glass furnace is a thermal redox reactor which converts a wide range of hazardous waste materials into simple non-hazardous compounds: chiefly carbon dioxide, calcium chloride, and inert stable glass.

The necessary high temperature is maintained electrically by passage of electric current through the glass between immersed electrodes. This is resistance heating; there is no arc.

Organic materials fed into the furnace are subjected to intense heat (2300° F) in the presence of air and water vapor. Chlorine is reduced to hydrogen chloride and converted to $CaCl_2$; carbon is oxidized to carbon dioxide; mineral residues are melted into glass.



A broad range of materials can be thermally destroyed (made non-hazardous):



- Asbestos
- Arc Furnace Dust
- Incinerator Ashes
- Contaminated Soil
- All Chloro Organics
- Paint Solvents and Sludges
- Electroplating Sludges
- Military Wastes

- Pot Liner from Aluminum
- Sludges from:
  - Water purification,
  - Municipal sewage
- * In-Plant wastes, all kinds
- Superfund remedial, including soil and lagoon mud